(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 237 259 A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 87301870.9

(22) Date of filing: 04.03.87

(51) Int. Cl.⁴: **H 01 J 49/42**

(30) Priority: 07.03.86 US 837600

(43) Date of publication of application:
16.09.87 Bulletin 87/38

(84) Designated Contracting States:
CH DE FR GB IT LI NL SE

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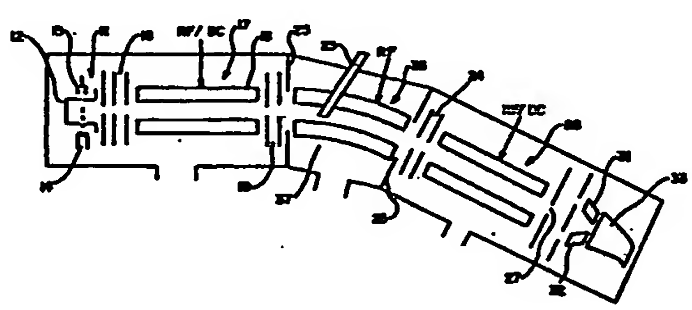
(54) **Mass spectrometer.**

(57) A mass spectrometer includes an ion source (11) for projecting ions along a predetermined path, a detector (31, 32, 33) offset from said path, a quadrupole ion filter or analyzer (26) disposed adjacent said detector (31, 32, 33) to provide its output to the detector, and quadrupole means (36) for directing ions away from said path into said ion filter and analyzer (26). Such a spectrometer produces relatively low noise levels.



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Description

MASS SPECTROMETER

This invention relates to a mass spectrometer, and more particularly to a low noise tandem quadrupole mass spectrometer.

Tandem quadrupole mass spectrometers are known, and have been used in the study of ion-molecule reactions. A center RF only quadrupole has been added to a tandem quadrupole mass spectrometer for study of photo dissociation and for metastable ion studies.

US-A-4234791 and US-A-4329582 disclose tandem quadrupole mass spectrometers including a highly efficient intermediate fragmentation stage which employs collision induced dissociation (CID) in the form of an RF only quadrupole.

All of the prior art tandem quadrupole mass spectrometers are noisy. It is believed that the noise is due to excited and fast neutral particles and fast ions traveling directly to the region of the detector where they strike surfaces in the vicinity of the detector and generate secondary ions. These secondary ions produce an interfering ion current which is detected by the detector.

According to this invention there is provided a mass spectrometer characterised by means for directing ions to be analyzed or filtered along a predetermined path; a quadrupole means for directing said ions away from said predetermined path; a quadrupole ion filter or analyzer for receiving the output of said quadrupole means; and detector means offset from said path and positioned to receive the output from said quadrupole ion filter or analyzer.

The invention provides an improved tandem quadrupole mass spectrometer having low neutral particle and fast ion noise.

The invention will now be described by way of example with reference to the drawings, in which:-

Figure 1 is a schematic view of a known tandem quadrupole mass spectrometer;

Figure 2 is a schematic view of a low noise tandem quadrupole mass spectrometer in accordance with the invention;

Figure 3 is a schematic view of another spectrometer in accordance with the invention;

Figure 4 is a schematic view of a known tandem sector quadrupole mass spectrometer;

Figure 5 is a schematic view of a tandem sector quadrupole mass spectrometer in accordance with the invention;

Figure 6 is a schematic view showing another embodiment of the tandem quadrupole spectrometer of Figure 2;

Figure 7 is a schematic view showing another spectrometer in accordance with the invention; and

Figure 8 is a schematic view showing a further spectrometer in accordance with the invention.

The known tandem quadrupole mass spectrometer shown in Figure 1 includes an ion source 11 shown as including a chamber 12 with an electron source 13 and collector 14. The ion source 11 may be operated in electron impact (EI) mode or chemical ionization (CI) mode. Other suitable types of ion sources used in mass spectrometry are those which generate secondary ions from a sample liquid matrix or solid sample by bombardment with a beam of fast atoms or ions. These ion sources are used for analysis of high mass organic compounds. There are other ionization techniques for use in elemental or inorganic mass spectrometry. These types of ion source provide more neutral particles and fast ions giving rise to higher noise levels. In any event, the ion source generates ions which are accelerated and directed in a predetermined path by lens 16 into the quadrupole mass filter or analyzer 17. Neutral particles and fast ions also travel to the quadrupole mass filter.

The quadrupole analyzer of filter 17 operates with a periodical voltage comprising an RF voltage and a d.c. voltage. The analyzer or filter 17 passes only ions of a selected charge to mass ration. That is, it filters the ions and only selects those having a charge to mass ratio within a predetermined range. The range is determined by the RF and d.c. voltages applied to the quadruopole rods 18. The ions which are not trapped or passed by the quadrupole filter or analyzer strike the walls of the enclosure or the qudrupole rods 18 and are neutralized. The selected or filtered ions pass through the analyzer 17.

A lens 19 focuses the ions of selected mass to charge ratio which are passed by the analyzer 17 into the quadrupole region 21 which includes rods 22 operated RF only. By operating the quadrupole RF only, it passes substantially all the ions, that is, it acts as a very broad band high pass filter.

The RF quadrupole 21 is in a separate volume defined by the walls 25 which also form part of the associated lens 19 and 24. A collision gas is introduced into the volume via a suitable inlet 23. The ions passed by quadrupole 21 collide with the gas to form daughters or fragments of the selected ions. The fragments or daughters are passed through lens 24 into a second quadrupole mass filter or analyzer 26 where particles of selected mass are selected and passed through the aperture 27 through the openings formed in the X-ray shield 28 to either dynodes 31 or 32 depending whether negative or positive ions are to be analyzed. The secondary ions or electrons leaving the dynodes are then collected by an electron multiplier 33 which provides an output signal. A preferred detector is described in US-A-4423324.

Operation of a tandem mass spectrometer including a collision induced dissociation region is described in US-A-4234791 and US-A-4329582.

As described above, a tandem quadrupole mass spectrometer of the type just described suffers from noise because of excited and fast neutral particles and fast ions which are generated in the ion source. It is believed that these neutral particles and fast ions travel in a straight line through the various

quadrupoles and lenses and strike surfaces in the vicinity of the dynodes 31, 32. When they strike these surfaces, they cause emission of positive and negative ions (possibly electrons) which are attracted by the dynodes 31 or 32 and sensed by multiplier 32 and detected as a signal. This noise seems to be strictly a line- of-sight phenomenon since it does not occur in magnetic sector instruments which have a magnetic field and an electrostatic sector and therefore have a curved ion path between the ion source and the detector. In these instruments the detector region is remote from the line of sight of the ion source.

In view of the above, it is proposed that in a triple tandem quadrupole system of the type described in Figure 1 noise would be reduced if the detector assembly were placed remote from the ion source ion path whereby neutral particles could not travel in a straight line to and strike surfaces adjacent the detector.

Figure 2 shows a triple tandem mass spectrometer in accordance with the present invention. Like reference numerals have been applied to parts which correspond to those in Figure 1.

In the spectrometer shown in Figure 2 the RF only quadrupole is bent as illustrated by quadrupole 36 so that the detector is no longer in line with the ion source 11. Neutral particles traveling in a straight line from the ion source 11 then strike either the walls of the enclosure or the quadrupole rods 37. Thus, any secondary particles are collected and dissipated, never finding their way to the vicinity of the detector. In summary, the excited neutrals impinge upon intervening surfaces and never reach the region of the detector where they can add to the signal. The neutrals are effectively filtered by the RF only quadrupole and never travel to the mass filter. Even if a secondary from an excited neutral would have a mass appropriate to allow it to traverse through the last quadrupole 26 to the detector, its initial position would most likely be such that its transmission through the quadrupole and to the detector would be highly unlikely.

The mass spectrometer of Figure 2 operates in the same manner as the prior art as the bent quadrupole acts like a straight one for the ions of interest.

Bent quadrupoles have been known for bending of ion beams. The book "Quadrupole Mass Spectrometry and its Applications" edited by Peter H. Dawson provides criteria for operation of a bent quadrupole ion beam guide. Generally, the radius of curvature of the axis of the quadrupole structure must be much larger than the characteristic dimension of the quadrupole electrode structure.

The theory of operation of quadrupoles and their ion transmission characteristics is well known and is described in US-A-2939952. Also the early chapters of the previously mentioned book "Quadrupole Mass Spectrometry and its Applications" discuss this subject in detail. In summary, there are two modes of operating a quadrupole: RF only and RF/DC. When only RF voltage is applied between rod pairs then, theoretically, the device will only transmit ions above some threshold or cutoff mass. When a combination of RF and DC voltages is applied between pole pairs there is both an upper cutoff mass as well as a lower cutoff mass. As the ratio of DC to RF voltage increases, the transmission band of ion masses narrows. The quadruple mass filter operation occurs when the applied ratio of DC to RF is such that the pass band of the device is so narrow as to allow only a single ion mass to transmit. The specific range of ion masses passed by the quadrupole is theorectically solely a function of the device characteristic dimension, r_0, the magnitudes of the applied RF and DC voltages, and the frequency of the applied RF. However, since real devices are of finite length, ion transmission also depends upon the velocity with which ions travel down the length of the quadrupole. If ions enter the device with axial velocities such that they do not experience a sufficient number of field cycles in transit through the quadrupole, some ions with masses outside the ion mass pass band will be transmitted anyway. In general the effect of increased axial ion velocity is a progressive widening and smearing of the ion mass pass band limits. At very high axial velocities ion transmission can become virtually independent of ion mass.

For a bent quadrupole as in Figure 2, the effect of axial velocity on ion transmission is substantially different from the straight quadrupole. At low axial velocities the strong focusing nature of the quadrupole field is sufficient to divert all ions within the pass band along the curved axis of the quadrupole. However, at higher axial velocities ions with masses near the limits of the pass band do not experience sufficient strong focusing to follow the curved ion path and are not transmitted. In general, for a curved quadrupole the effect of increased axial ion velocity is a progressive narrowing and smearing of the ion mass pass band limits. At very high axial ion velocities no ions can be transmitted. Naturally the larger the radius of curvature of the device the slower the onset of this velocity discrimination effect. A gently curved structure like the RF only quadrupole in Figure 2, operating with a conventional frequency, RF voltage, and range of ion axial velocities behaves substantially like a straight one. However, its curvature is sufficient such that very fast ions, which are sometimes part of the noise problem, are not transmitted.

A spectrometer in accordance with the invention can otherwise include only a single mass filter or analyzer such as the mass spectrometer shown in Figure 3 wherein like reference numerals have been applied to like parts. In this mass spectrometer the first tandem analyzer or filter stage of Figure 2 has been eliminated.

The bent quadrupole 36 could be operated such that it is both a neutral noise filter and an ion prefilter for the mass analyzer. Appropriate RF/DC voltages are applied to the bent quad such that only a broad band of ions around the ion mass being analyzed in the mass filter are allowed to reach the mass filter 26.

This is a particularly appropriate mode of operation when the ion source emits an ion beam that consists overwhelmingly of one or a few ion masses. Independent of neutral noise there is an interfering noise current at the detector that is associated with

the magnitude of the total ion current entering the mass analyzer. Elimination of the dominant ion masses from the ion beam in the bent quadrupole prior to its entrance to the quadrupole mass analyzer should commensurately diminish this ion current related noise and thus enhance the detection and measurement of important but weak component ion masses.

The bent quadrupole can be used in other tandem mass spectrometers such as those used for study of photo dissociation and metastable ion structures.

One such tandem mass spectrometer is a hybrid sector quadrupole instrument. A simplified known hybrid sector quadrupole instrument of BEQQ geometry is shown in Figure 4. Essentially this instrument performs the same function as the tandem quadrupole instrument in Figure 1, only a high resolution double focusing sector mass analyzer has been substituted in place of the first quadrupole mass filter, 17. Like reference numerals have been assigned to parts that correspond to those in Figure 1. The high resolution analyzer 79 consists of entrance slit 71, α- slit 72, magnetic sector 73, β- slit 78, electrostatic sector 74, and exit slit 75. The ions created in the ion source 11 are mass analyzed at high resolution and the parent ion beam exits at the exit slit 75. At this point there are two possible experiments that can be performed: Low energy CID and high energy CID. The low energy CID experiment is the same experiment that is performed with the instrument in Figure 1. The parent ion beam is transmitted through and decelerated in the deceleration lens system 77 into a conventional RF quadrupole collision cell 21 where it undergoes low energy CID at kinetic energies ranging from 2 to 200 eV. The daughter ions are in turn mass analyzed in the RF/DC quadrupole mass analyzer and detected at the detector. This experiment is very quiet as the noise causing particles generated in the ion source, as discussed before, do not transmit through the sector analyzer.

The other experiment, high energy CID, is not as quiet. In this experiment the parent ion beam undergoes CID in a needle collision cell, 76, at a kinetic energy of thousands of volts prior to entering the deceleration lens. This collision cell consists of a capillary tube 80 that introduces a jet of collision gas to the parent ion beam. The daughter ions produced in this region are decelerated in the deceleration lens and are transmitted through the RF only quadrupole into the mass analyzing quadrupole for mass analysis and then detected. The high energy collision process generates a couple of particle entities that can produce substantial noise at the detector. Neutral daughter fragments are created with high kinetic or internal energies. These neutrals can transmit directly to the region of the detector in a line-of-sight fashion and produce noise causing secondaries. Also the daughter ions have well defined but widely spread kinetic energies. The kinetic energy of the parent ion is distributed to its ionic and neutral daughter fragments in proportion to their masses. Low mass daughter ions may have hundreds or thousands of electron volts less kinetic energy than higher mass daughters of the same parent. So when a low mass daughter ion is decelerated to a velocity appropriate for mass analysis in the quadrupole mass filter other higher mass daughter ions present will still have very high kinetic energies and may transmit through the quadrupoles at such a high velocity that they are not effec tively mass analyzed. These fast daughters can produce a very substantial interfering noise current at the detector. While this noise can be taken care of by the addition of a kinetic energy analyzing means prior to the quadrupole mass analyzer, this causes an increase in complexity and often a decrease in sensitivity of the instrument. Substitution of a bent quadrupole for the straight quadrupole in the low energy collision cell would be a simple means by which to eliminate both the neutral and fast daughter ions generated during high energy CID. Figure 5 shows a BEQQ geometry hybrid instrument with a bent quadrupole deposed as the low energy collision cell. Like reference numerals have been applied to parts which correspond to those in Figures 2 and 4. In the high energy CID mode an RF voltage or combination of RF and DC voltages is applied to the bent quadrupole as to efficiently transmit the particular mass daughter ion being analyzed in the quadrupole mass analyzer while accentuating the velocity filtering characteristic of the bent quadrupole so as to prevent any fast higher mass daughter ions from transmitting. The excited and fast neutrals emitted from the high energy collision cell will also be removed from the beam as they will not be diverted toward the mass analyzer and detector by the curved quadrupole. In the low energy CID mode the bent quadrupole is operated RF only and as discussed above behaves like a straight RF only collision cell.

In the RF/DC or in an RF only mode, the bent quadrupole reduces the number of neutral particles or fast ions which reach the detector region of the mass spectrometer and thereby reduces the neutral noise caused by secondary ions generated in the vicinity of the detector.

Although a bent quadrupole RF only stage is preferred, a straight quadrupole stage 41 disposed at an angle will perform to minimize the travel of neutral particles and fast ions from the ion sources to the detector. Figure 6 shows a mass spectrometer as in Figure 2 with like reference numerals. However, the RF quadrupole stage includes straight rods 41 at an angle with respect to the rods of the quadrupole 17.

The mass spectrometer may use one or more bent or angled sections to provide enhanced noise immunity. Figure 7 shows a system using three RF sections 46, 47 and 48, two of which are curved and one of which is straight. The center straight section 47 may have a gas inlet 49 and perform in the CID mode. The RF only quadrupole may be composed of combined straight and curved sections. Figure 8 shows a mass spectrometer including an RF section having outer straight sections 52 and 53 separated from a CID section 54 which includes a curved rod portion 56 and a straight portion 57.

It is apparent that there are many combinations of quadrupole filters or analyzers and RF only sections,

CID or otherwise, possible. In common with all is the fact that the detector is offset from the ion source whereby there is no direct transmission or travel of neutral particles or fast ions.

Claims

1. A mass spectrometer characterised by means for directing ions to be analyzed or filtered along a predetermined path; a quadrupole means (36) for directing said ions away from said predetermined path; a quadrupole ion filter or analyzer (26) for receiving the output of said quadrupole means (36); and detector means (31, 32, 33) offset from said path and positioned to receive the output from said quadrupole ion filter or analyzer (26).

2. A mass spectrometer as claimed in Claim1 characterised by an ion filter or analyzer (17) for receiving said ions from an ion source (11) and providing output ions within a selected mass-to-charge ratio range, said quadrupole means (36) receiving the output of said ion filter or analyzer (17).

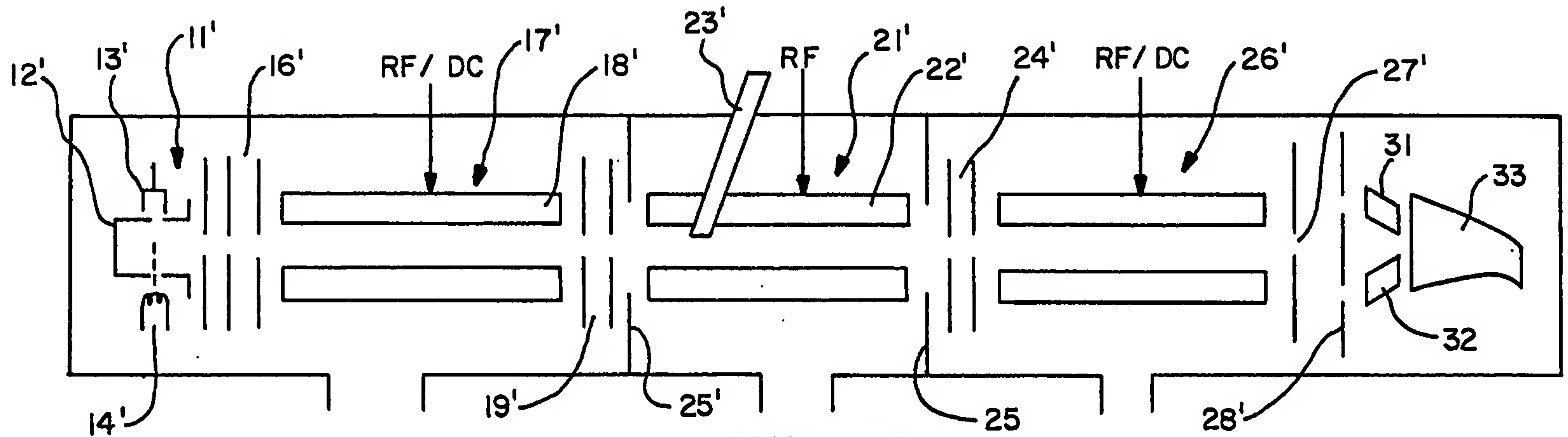
3. A mass spectrometer as claimed in Claim 1 or Claim 2, characterised by means for applying both an RF and a DC signal to said quadrupole means (36).

4. A mass spectrometer as claimed in Claim 1, Claim 2 or Claim 3, characterised in that said quadrupole means (36) includes bent quadrupole rods (37).

5. A mass spectrometer as claimed in Claim 1, Claim 2 or Claim 3, characterised in that said quadrupole means (36) includes straight rods (41) at an angle with respect to said path.

6. A mass spectrometer as claimed in Claim 1, Claim 2 or Claim 3, characterized in that said quadrupole means (36) includes straight (47; 57) and bent (46, 48; 56) rods.

7. A mass spectrometer as claimed in any preceding claim, characterised by means (23; 49) for introducing a collision gas into said quadrupole means (36).



PRIOR ART

FIG. — 1

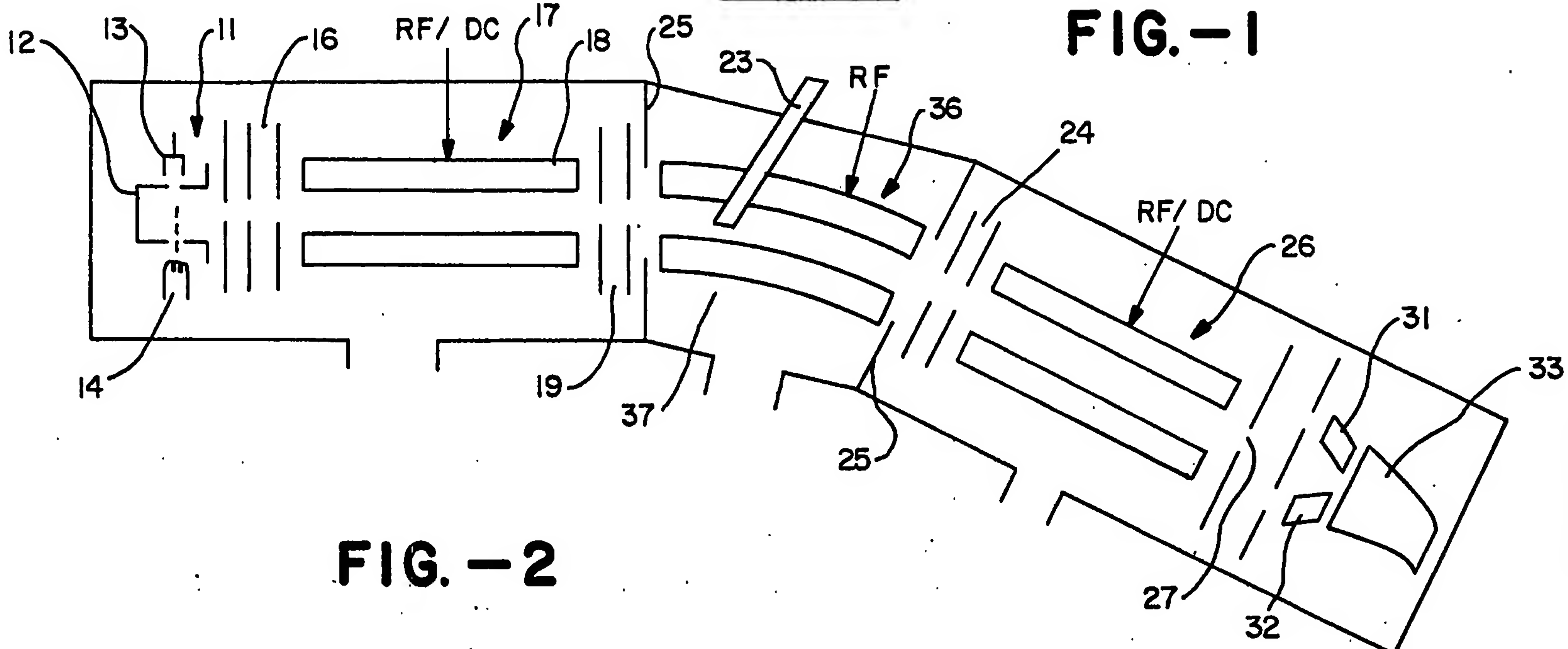


FIG. — 2

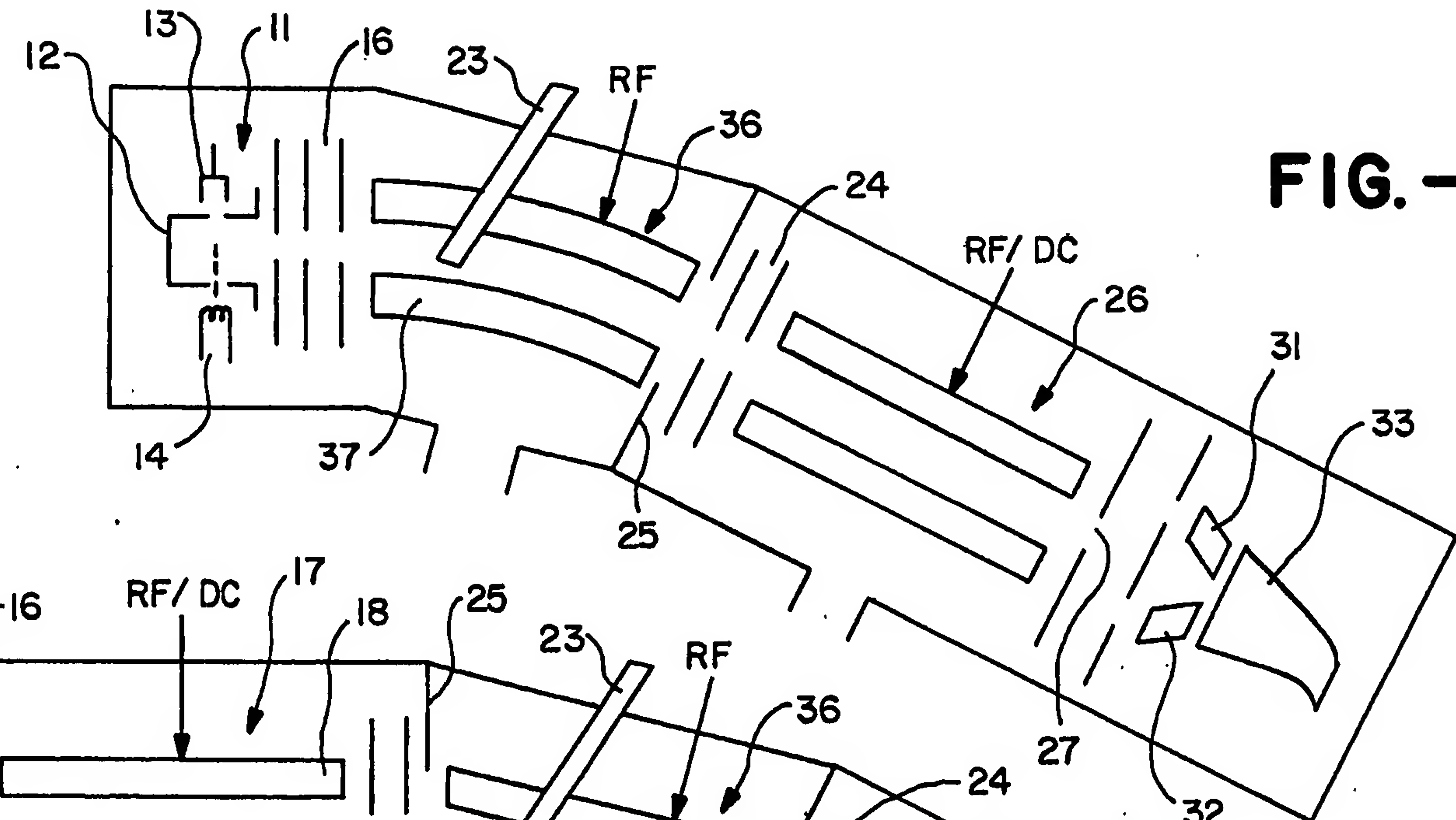


FIG.—3

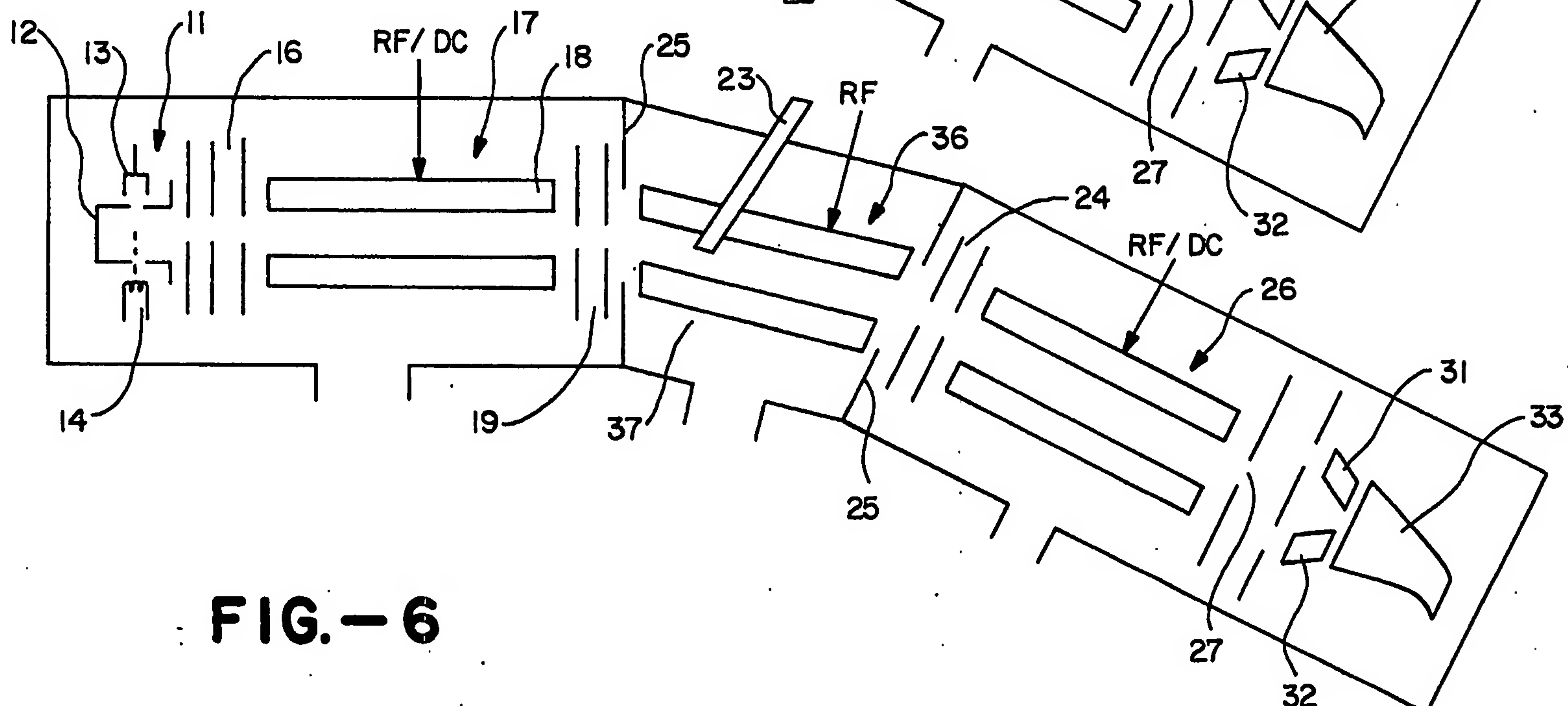


FIG.—6

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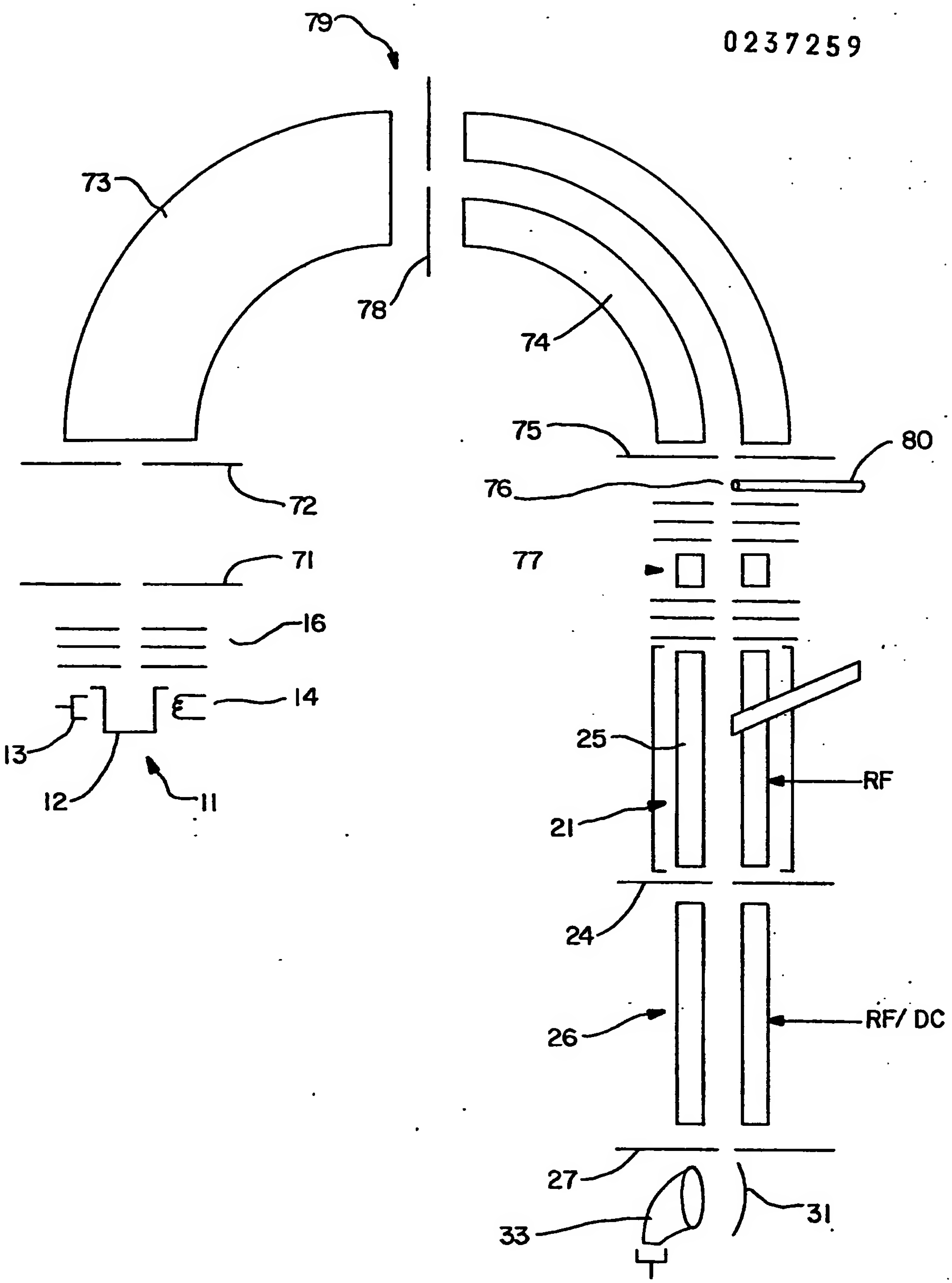
79
73
78
74
75
80
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RF
12
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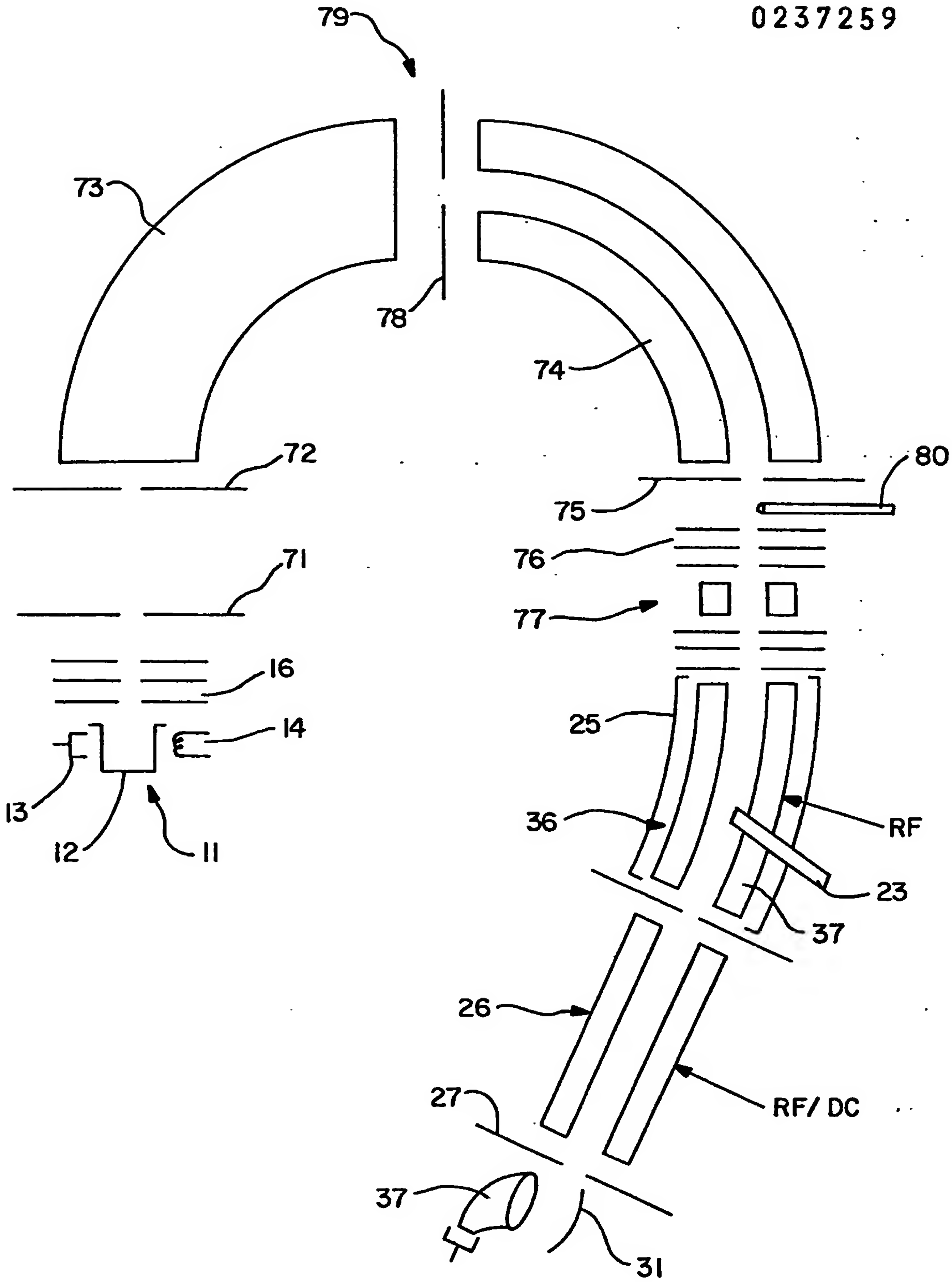
RF/ DC
27
33
31

FIG. —4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RF
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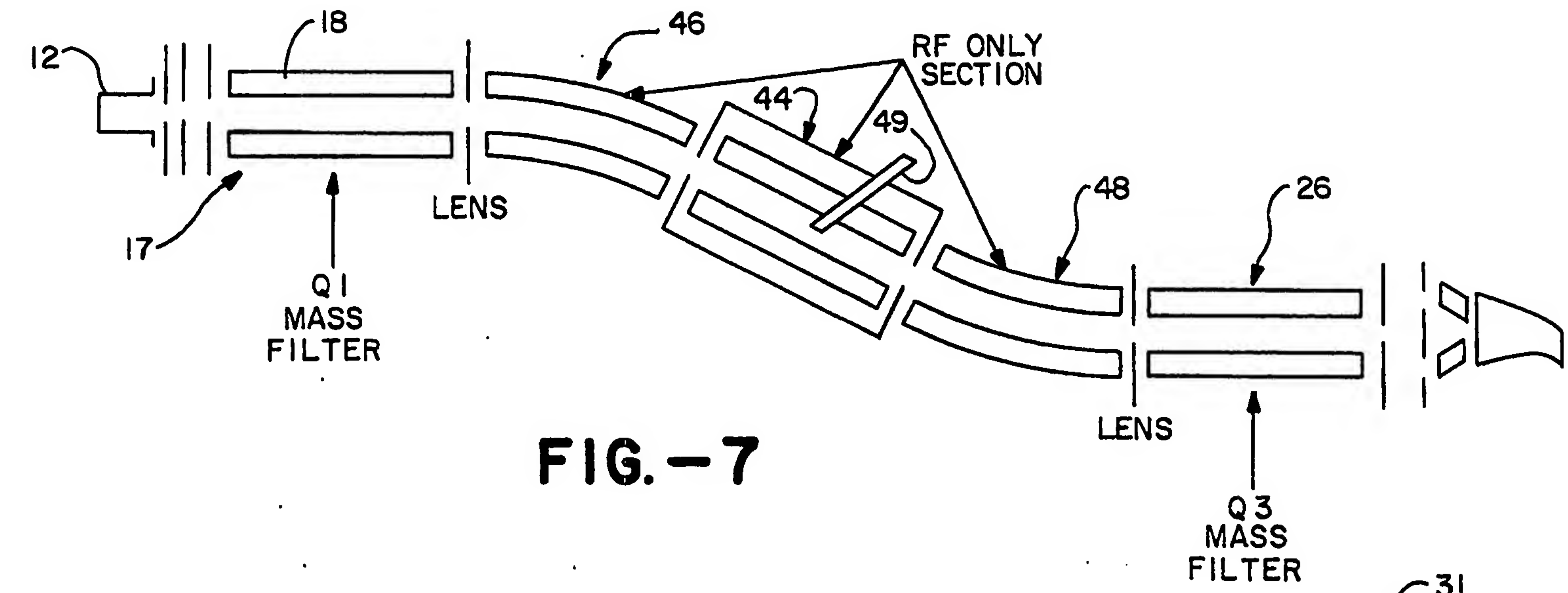
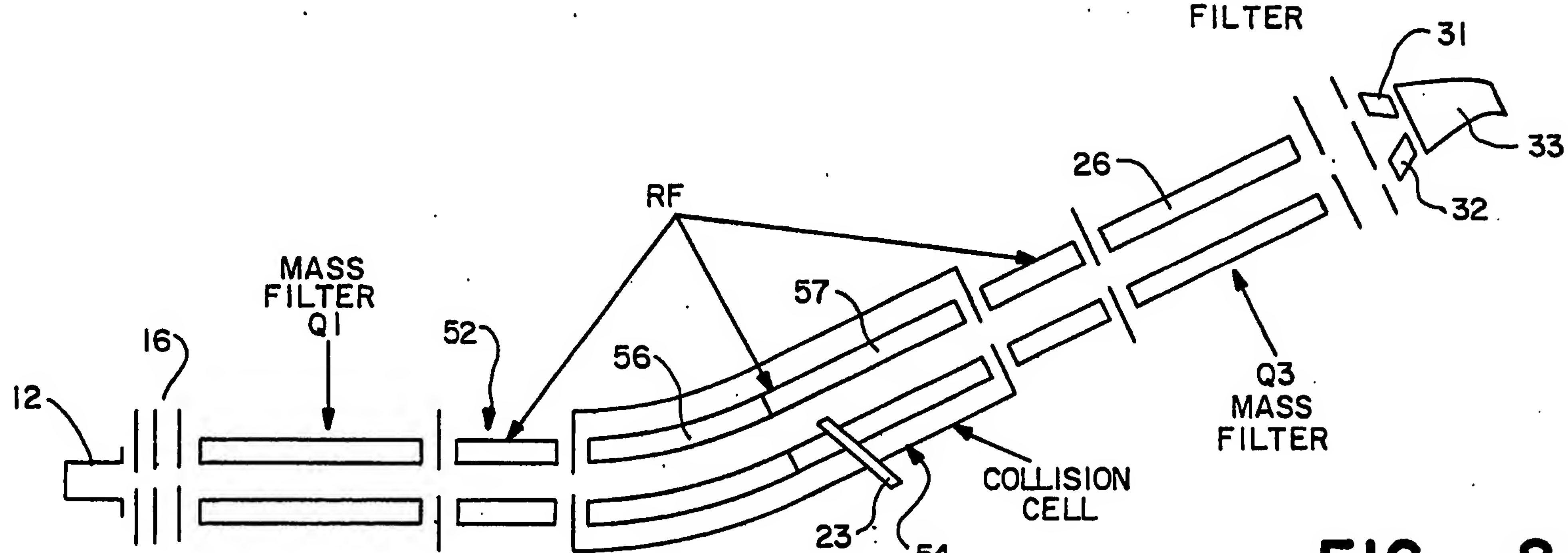
RF/ DC
37
31

FIG. — 5



12
18
46
RF ONLY SECTION
44
49
48
26
17
Q1 MASS FILTER
LENS
LENS
Q3 MASS FILTER

FIG. — 7



31
33
32
26
RF
MASS FILTER Q1
57
16
52
56
12
Q3 MASS FILTER
COLLISION CELL
23
54

FIG. — 8